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Sulphated tin oxide (STO)-catalyzed synthesis of arylated vinyl ethers

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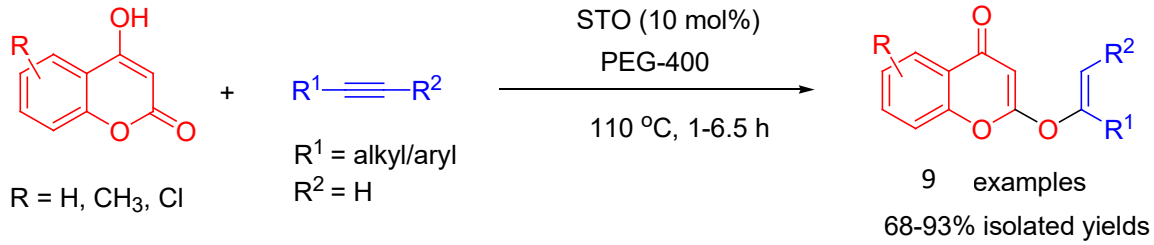
C H R O N I C L E

Article history:
Received October 3, 2024
Received in revised form
November 2, 2024
Accepted February 7, 2025
Available online
February 7, 2025

Keywords:
Sulphated tin oxide (STO)
4-hydroxycoumarine (4-HC)
Alkynes
Vinyl ethers
PEG 400
Recyclability and catalysis

A B S T R A C T

The *C3* or *O*-alkylation of 4-hydroxycoumarin (formation of new C-C and C-O bond) is undoubtedly one of the most important and challenging reactions in synthetic chemistry due to its pharmaceutical utility. In this communication, we report sulfated tin oxide (STO)-catalyzed synthesis of arylated vinyl ethers in moderate to good isolated yields (68-93%) from the reaction of substituted phenyl acetylenes (terminal alkynes) with 4-hydroxy coumarin in polyethylene glycol (PEG 400) as solvent at 110 °C. The catalyst can be recycled up to 5 times without losing the significant yield.



Graphical Abstract

1. Introduction

Coumarin and its derivatives are important heterocycles from a pharmacological standpoint. Because of their pharmacological and biological properties, including their anticoagulant, anti-HIV, and antifungal properties, coumarin and its derivatives are the subject of much research.[1-5] Coumarin is an essential ingredient in a number of natural products.[6-7] Furthermore, functionalized coumarin derivatives are widely employed as anticancer and antibacterial medications, which have a vast array of uses in biological science.[8] Many functionalized coumarin derivatives have been the focus of design and synthesis efforts in the realm of medicinal chemistry due to its unique physicochemical characteristics.[9-10]

4-Hydroxycoumarin is a significant member of the coumarin family due to its structure and chemical behavior, which have greatly influenced organic synthesis (**Fig. 1**).[11-16] Not only are they important synthetic endpoints, but they also form the structural core of many natural products, which has increased interest in them. Additionally, there are increasing reports

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doi: 10.5267/j.ccl.2025.2.001

on the investigation of 4-hydroxycoumarin derivatives as ligands of transition metals and rare earth element metal complexes that exhibit bioactivities of their own, such as fluorescence, etc.[17-19]

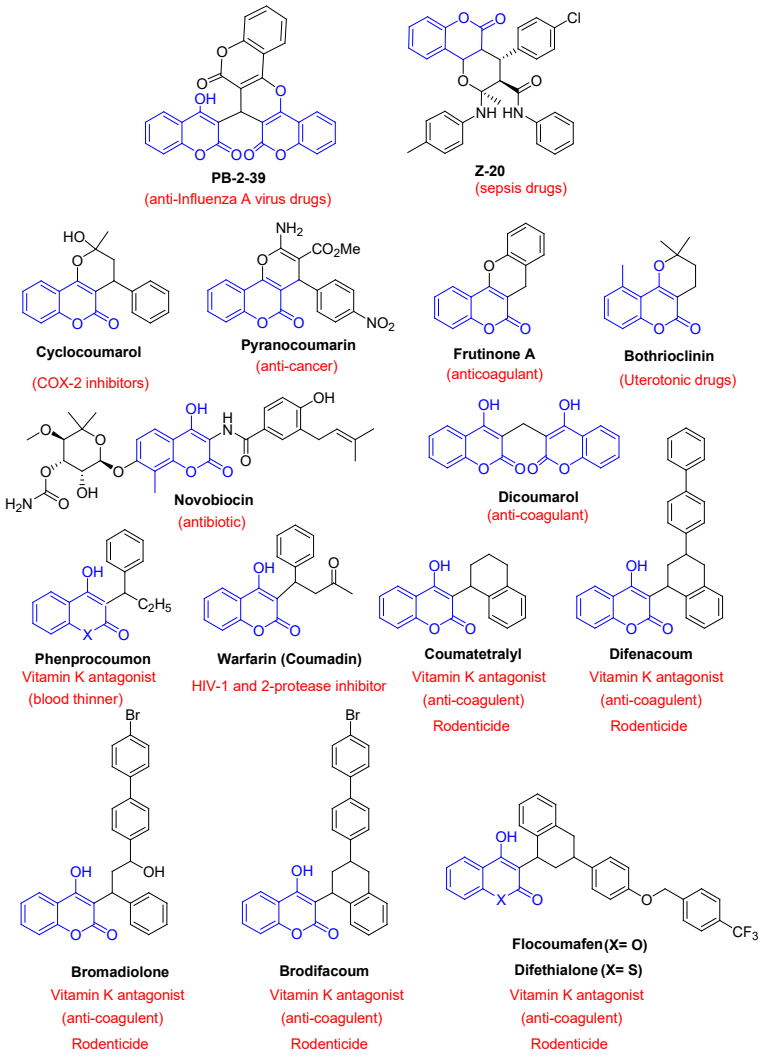


Fig. 1. Representative 4-hydroxycoumarins in market

The reactions involving 4-hydroxycoumarin based on the literature review show great regioselectivity, and their progression is readily regulated by altering the starting compounds' molecules' substituents and reaction conditions.[20] The three tautomeric structures of 4-hydroxy-2*H*-chromen-2-one (**Fig. 2**), which are the tautomeric keto-enol forms, 4-hydroxy-2-chromenone (I), 2,4-chromandione (II), and 2-hydroxy-4-chromenone (III), greatly regulate its reactivity. The phenomenon of proton shifting in the three tautomeric structures has been thoroughly studied using spectroscopic, thermochemical, computational, and other chemical reactivities. Both nucleophilic and electrophilic sites can be found in the structure of 4-hydroxycoumarin. Different kinds of nucleophiles can replace the carbon atom that is attached to the hydroxyl group, and this can result in a number of reactions, such as arylation, amination, and halogenations. The nucleophilicity of the carbon atom behind the carbonyl group is the most important component of the 4-hydroxycoumarin moiety.

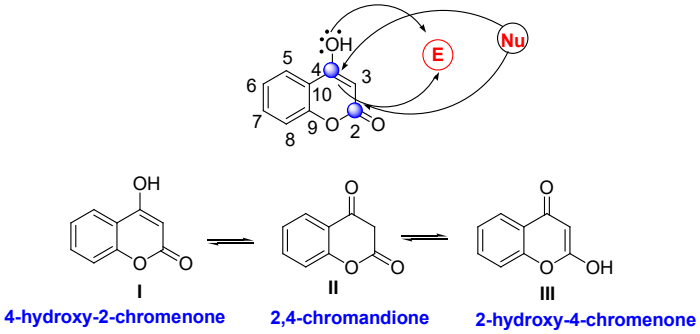


Fig. 2. Tautomeric and active centres of 4-hydroxycoumarin

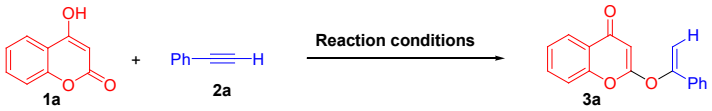
The carbonyl carbon is preferentially accessed by the comparatively mild nucleophiles. Several techniques have been documented where the hydroxyl group's oxygen atom functions as an excellent nucleophile and is targeted by acylating and alkylating chemicals. As previously indicated, the *C3* or *O*-alkylation of 4-hydroxycoumarin (creation of new C-C and C-O bonds) is unquestionably one of the most significant and difficult reactions in synthetic chemistry because of its potential for pharmacological applications. Therefore, a stronger catalyst that will activate the OH group of 4-hydroxycoumarin and increase their susceptibility to nucleophilic attack under mild circumstances is desperately needed. The ideal catalyst should be easily accessible, affordable, less hazardous, and capable of operating in an environmentally friendly way in order to meet the requirements of green chemistry. This will stimulate curiosity about the possible benefits and broad applications of the resultant target compounds.

In synthetic chemistry, solid heterogeneous catalysts are recognized to provide expected benefits such as easy regeneration, reduced corrosiveness, affordability, ease of handling, and efficient reusing.[21] Because of its huge surface area, high efficiency, non-corrosive nature, low cost, and wide surface area, sulfated tin oxide, commonly known as SO_4^{-2}/SnO_2, has gained popularity and efficiency as a catalyst. Composed of sulfated and sulfonic acid moieties on a range of heterogeneous solid bases, it is extensively used in chemical and industrial settings.[22-42] We have just now been able to successfully utilize STO's applications in the synthesis of β-amino alcohols and 4-aryl-NH-1,2,3-triazoles.[41-42] Following Majee and colleagues' initial discovery of this type of *O*-alkylation at the C2 atom of 4-HC, we describe here the effective synthesis of arylated vinyl ethers in keeping with our attempts to develop novel methodologies.[43]

The use of atom-efficient catalytic processes in the manufacturing of pharmaceuticals and fine chemicals has attracted attention as the pressing need for more sustainable, greener technologies becomes increasingly apparent. One such component that is receiving increasing attention is the use of alternative reaction media, which circumvents the problems associated with many of the traditional volatile organic solvents. Over time, a variety of suitable and eco-friendly alternative reaction media have been studied, such as supercritical fluids, ionic liquids, and polyethylene glycol.[44-46] According to this perspective, polyethylene glycol (PEG) functions as an environmentally friendly solvent and alternative reaction medium.[47-52] PEG has been studied as a solvent for chemical synthesis for more than 20 years. PEG is frequently used in chemical synthesis instead of hazardous organic solvents because of its biodegradable, biocompatible, non-toxic, and benign properties. PEG has reportedly been utilized as a solvent in a number of heterocyclic molecule synthesis processes, oxidations and reductions, heteroatom-heteroatom bond-forming events, and carbon-carbon and heteroatom-heteroatom bond-forming reactions.[53-62]

2. Results and Discussion

In continuation of our efforts in the development of C-C and C-heteroatom bond formation reactions,[41-42, 63] we have studied the reaction of 4-hydroxycoumarin (**1a**) and phenyl acetylene (**2a**) in a variety of solvents was the first step in the investigation (**Scheme 1**).

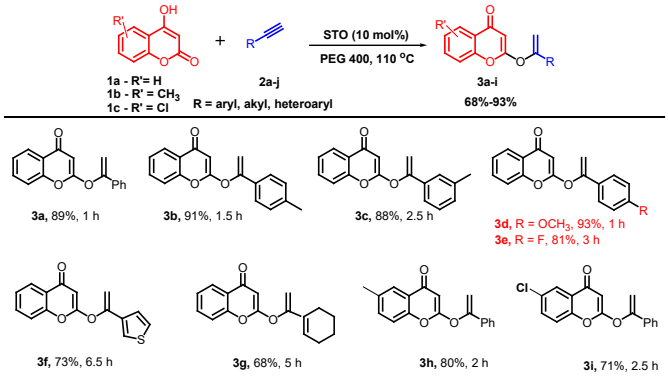


Entry	Catalyst (mol%)	Solvent	Temp (0 °C)	Yield (%)
1	SnO_2 (20 mol%)	CH_3CN	80	NR
2	STO (20 mol%)	CH_3CN	80	65
3	STO (20 mol%)	toluene	110	78
4	STO (20 mol%)	$CHCl_3$	reflux	38
5	STO (20 mol%)	THF	reflux	23
6	STO (20 mol%)	neat	110	17
7	STO (20 mol%)	PEG 400	110	90
8	**STO (10 mol%)**	**PEG 400**	**110**	**89**
9	STO (5 mol%)	PEG 400	110	56

Scheme 1. Optimization of the reaction conditions

In the target reaction, tin oxide was found to be ineffective (entry 1). The reaction was first conducted using 20 mol% STO in CH_3CN at 80 °C with ambient air. Fortunately, after a brief reaction period of one hour, the product, 2-((1-phenylvinyl)oxy)-4*H*-chromen-4one (**3a**), was obtained in good yield (65%) (entry 2). Motivated by this outcome, we conducted a number of reactions to improve the reaction circumstances; **Scheme 1** provides a summary of the outcomes. Common solvents including acetonitrile, THF, and $CHCl_3$ were initially used in the procedure, however the yields of the

intended products were lower (entries 2, 4, and 5). The intended product has a 78% isolated yield in toluene (entry 3). The reaction yield (entry 6) indicates that the reaction was ineffective when there was no solvent present. To our surprise, the yield of the intended product rose significantly (entry 8, 89%) when the reaction was carried out using 10 mol% STO in PEG 400. In contrast to the reaction condition from entry 8, altering the catalyst loading (entries 7 and 9) did not improve the reaction yield. The substrate scope of this protocol was examined when the optimal reaction conditions (10 mol% STO in PEG 400 at 110 °C in air) were determined. We concentrated on how different terminal alkynes interacted with 4-hydroxycoumarin (**1a**) (**Scheme 2**). Excellent yields of the required products (**3b-d**) were obtained by substituting electron-donating groups (CH_3, OCH_3) into phenyl acetylenes. With an electron-withdrawing substituent, phenol acetylene yielded the intended product **3e** in a high yield of 81%. Furthermore, at the ideal reaction circumstances, terminal alkyne replaced with a heterocyclic moiety also performed well (**3f**, 73%). Notably, aliphatic alkynes **2g** also reacted well with **1a**, yielding good yields (68%) of the corresponding products **3g**.



Scheme 2. Substrate scope of the reaction between 4-hydroxycoumarin and alkyne

In addition, we have exploited the utility of substituted 4-hydroxycoumarins (**1b** and **1c**) to establish the general applicability of the reaction conditions and the desired products were obtained in good yields (**3h**, 80%; **3i**, 71%). The mild reaction conditions prevent the products from breaking down or the starting materials from polymerizing. The recycling of the STO catalyst in the reaction between 4-HC (**1a**) and phenyl acetylene (**2**a) was then examined (**Fig. 3**). After the reaction was finished, the STO was cleaned with diethyl ether, and the solution was vacuum-filtered through a glass funnel that had been sintered. Immediately after drying, the recovered catalyst was used once more without requiring additional purification. The catalyst may be extracted and used up to five additional times without seeing a discernible decrease in its catalytic activity (85% isolated yield for **3a** after the fifth run).

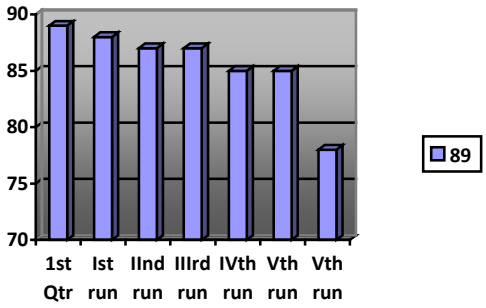


Fig. 3. Reusability chart of STO for the compound **3a**

In summary, using STO under mild reaction conditions has resulted in *O*-vinylation of 4-hydroxycoumarin from the reaction of 4-hydroxycoumarin and alkynes. Using this atom-efficient approach, a small library of 2-(vinyloxy)-4*H*-chromen-4-one derivatives (**3**) has been synthesized. PEG was determined to be the ideal solvent of choice to execute the reaction during optimization. Notable benefits of the current procedure include its rapid reaction time, recyclable heterogeneous catalyst and tolerance for a broad variety of functional groups.

3. Experimental procedure

A Bruker 400 (400 MHz) spectrometer was used to determine the ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$. The signals are recorded as s (singlet), d (doublet), t (triplet), and m (multiplet), while the coupling constants J are supplied in Hz. Chemical shifts are indicated in parts per million (ppm, δ). A glass slide coated with silica gel (Merck, Silica gel G for TLC) was used for TLC. For column chromatography, silica gel (60-120 mesh) was utilized. Prior to usage, every solvent

was dried and distilled. All of the starting materials, including terminal alkynes **2** and 4-hydroxycoumarin **1a**, substituted 4-hydroxycoumarins (**1b** and **1c**), as well as other reagents, catalysts, and solvents, were acquired from commercial vendors such as Spectrochem Chemicals, Sigma-Aldrich, and Merck.

General procedure for the synthesis of 3a-i

A mixture of 4-hydroxycoumarin, **1a** or substituted 4-hydroxycoumarins, **1b-c** (1 mmol), terminal alkyne **2** (1 mmol) and STO (10 mol%) in PEG-400, stirred at 110 °C for the time specified. Following the conclusion of the reaction, which was observed by thin-layer chromatography, the mixture was diluted with anhydrous diethyl ether and allowed to stir for fifteen minutes. Subsequently, the layers were allowed to separate and the ether layer was decanted. The mother liquor (PEG) was set aside for subsequent runs, and this procedure was performed twice to provide the crude products in diethyl ether. Following solvent evaporation, the crude product was refined using column chromatography on silica gel with 1:1 petroleum ether/ethyl acetate to produce the pure corresponding products (**3a-i**).

Spectral data for the synthesized compounds

2-((1-Phenylvinyl)oxy)-4*H*-chromen-4-one (3a): 89%, light yellow solid; mp. 59-61 °C. IR (KBr): 1680 (-C=O), 1221 (-C-O) 832, 751 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.13-8.15 (m, 1 H, Ar), 7.63-7.67 (m, 1 H, Ar), 7.53-7.56 (m, 2 H, Ar), 7.35-7.46 (m, 5 H, Ar), 5.70 (s, 1 H, -C<u>H</u>=), 5.55 (d, *J* = 2.8 Hz, 1 H, -C<u>H</u>$_2$), 5.21 (d, *J* = 2.8 Hz, 1 H, C<u>H</u>$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.40 (-<u>C</u>=O), 166.37, 154.29, 153.89, 133.57, 132.43, 129.96, 129.02, 125.95, 125.60, 125.34, 123.05, 117.50, 102.39 (-<u>C</u>H$_2$=), 91.06 (-<u>C</u>H=).
2-((1-(*p*-Tolyl)vinyl)oxy)-4*H*-chromen-4-one (3b): 91%, yellow gum. IR (KBr): 1637, 1373, 1060, 616 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.12 (m, 1 H), 7.67–7.62 (m, 1 H), 7.45–7.37 (m, 4 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 5.69 (s, 1 H), 5.49 (d, *J* = 2.8 Hz, 1 H), 5.14 (d, *J* = 2.8 Hz, 1 H), 2.34 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.37 (-<u>C</u>=O), 166.45, 154.41, 153.90, 140.16, 133.51, 129.69, 129.63, 125.94, 125.55, 125.29, 123.08, 117.49, 101.47 (-<u>C</u>H$_2$=), 91.01 (-<u>C</u>H=), 21.41 (CH_3).
2-((1-(*m*-Tolyl)vinyl)oxy)-4*H*-chromen-4-one (3c): 88%, yellow gum. IR (KBr): 1684, 1274, 816, 768 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.13 (m, 1 H), 7.67–7.63 (m, 1 H), 7.46–7.34 (m, 4 H), 7.27–7.23 (m, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 5.70 (s, 1 H), 5.52 (d, *J* = 2.8 Hz, 1 H), 5.17 (d, *J* = 2.8 Hz, 1 H), 2.35 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.39 (-<u>C</u>=O), 166.44, 154.49, 153.91, 138.76, 133.53, 132.42, 130.78, 128.90, 125.99, 125.94, 125.56, 123.10, 122.52, 117.50, 102.23, 91.01, 21.57 (CH_3).
2-((1-(4-Methoxyphenyl)vinyl)oxy)-4*H*-chromen-4-one (3d): 93%, yellow gum. IR (KBr): 1685, 1260, 832, 763 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.13 (m, 1 H), 7.67–7.62 (m, 1 H), 7.49–7.37 (m, 4 H), 6.89–6.87 (m, 2 H), 5.71 (s, 1 H), 5.41 (d, *J* = 2.4 Hz, 1 H), 5.08 (d, *J* = 2.8 Hz, 1 H), 3.81 (s, 3 H, -OC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.40 (-<u>C</u>=O), 166.51, 160.92, 154.18, 153.93, 133.52, 126.89, 125.96, 125.56, 124.97, 123.10, 117.49, 114.39, 100.38, 91.02, 55.50 (O<u>C</u>H$_3$).
2-((1-(4-Fluorophenyl)vinyl)oxy)-4*H*-chromen-4-one (3e): 81%, yellow gum. IR (KBr): 1685, 1229, 833, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.13 (m, 1 H), 7.67–7.63 (m, 1 H), 7.56–7.52 (m, 2 H), 7.44–7.38 (m, 2 H), 7.08–7.04 (m, 2 H), 5.70 (s, 1 H), 5.48 (d, *J* = 2.8 Hz, 1 H), 5.17 (d, *J* = 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.33 (-<u>C</u>=O), 166.13, 164.90, 162.41, 153.90, 153.46, 133.64, 128.72, 127.40, 125.97, 125.67, 123.04, 117.48, 116.14, 102.0, 91.18.
2-((1-(Thiophen-3-yl)vinyl)oxy)-4*H*-chromen-4-one (3f): 73%, brown gum. IR (KBr): 1695, 1275, 949, 747 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.17–8.14 (m, 1 H), 7.68–7.64 (m, 1 H), 7.46–7.39 (m, 3 H), 7.35–7.33 (m, 1 H), 7.24–7.22 (m, 1 H), 5.77 (s, 1 H), 5.42 (d, *J* = 2.8 Hz, 1 H), 5.11 (d, *J* = 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.46 (-<u>C</u>=O), 166.42, 153.91, 150.60, 134.58, 133.61, 127.32, 125.97, 125.65, 124.95, 123.35, 123.08, 117.52, 101.35, 90.84.
2-((1-(Cyclohex-1-en-1-yl)vinyl)oxy)-4*H*-chromen-4-one (3g): 68%, yellow gum. IR (KBr): 1680, 1220, 828, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.16–8.14 (m, 1 H), 7.65–7.61 (m, 1 H), 7.43-7.36 (m, 2 H), 6.12 (t, *J* = 8.4 Hz, 1 H), 5.67 (s, 1 H), 5.03 (d, *J* = 2.4 Hz, 1 H), 4.9 (d, *J* = 2.4 Hz, 1 H), 2.19–2.16 (m, 2 H), 2.12–2.08 (m, 2 H), 1.73–1.67 (m, 2 H), 1.60–1.54 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.60 (-<u>C</u>=O), 167.27, 155.13, 153.84, 133.41, 128.78, 128.00, 125.86, 125.45, 123.07, 117.44, 100.56, 89.65, 25.40, 24.85, 22.22, 21.71.
6-Methyl-2-((1-phenylvinyl)oxy)-4*H*-chromen-4-one (3h): 80%, yellow gum. IR (KBr): 1681, 1275, 815, 772 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (d, *J* = 1.6 Hz, 1 H), 7.56–7.53 (m, 2 H), 7.46–7.43 (m, 1 H), 7.37–7.32 (m, 4 H), 5.69 (s, 1 H), 5.54 (d, *J* = 2.4 Hz, 1 H), 5.18 (d, *J* = 2.8 Hz, 1 H), 2.43 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.56 (-<u>C</u>=O), 166.32, 154.38, 152.13, 135.58, 134.65, 132.54, 129.94, 129.00, 125.40 (2C), 122.72, 117.22, 102.22, 91.04, 21.00 (CH_3).
6-Chloro-2-((1-phenylvinyl)oxy)-4*H*-chromen-4-one (3i): 71%, yellow gum. IR (KBr): 1682, 1261, 817, 771 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.10 (d, *J* = 2.4 Hz, 1 H), 7.60–7.57 (m, 1 H), 7.55–7.52 (m, 2 H), 7.41–7.36 (m, 4 H), 5.71 (s, 1 H), 5.56 (d, *J* = 2.8 Hz, 1 H), 5.20 (d, *J* = 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.06 (-<u>C</u>=O), 166.52, 154.38, 152.18, 133.69, 132.34, 131.66, 130.10, 129.09, 125.56, 125.36, 124.22, 119.15, 102.48, 91.09.

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